



Near-infrared to visible photon transition by upconverting NaYF₄: Yb³⁺, Gd³⁺, Tm³⁺ @Bi₂WO₆ core@shell composite for bisphenol A degradation in solar light

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ABSTRACT

The effective use of sunlight by photocatalyst systems is challenging. Here, we report an active-core@inert-shell nanohybrid composite that converts incompatible near-infrared (NIR) radiation to functional ultraviolet-visible (UV–vis) photons. The active core is composed of NaYF₄: Yb³⁺, Gd³⁺, and Tm³⁺ upconverting nanoparticles (UCNPs). An inert bismuth tungstate (Bi₂WO₆) shell with a narrow band gap (2.65 eV) was grown over the core via ethylenediaminetetraacetic acid-metal complex formation. Solar infrared photons were successfully converted to UV–vis photons, which activated the Bi₂WO₆ shell via Förster resonance energy transfer (FRET). The high UV–vis–NIR response of the UCNP@Bi₂WO₆ composite was demonstrated by 94% degradation of Bisphenol A in 180 min. Integrating UCNPs with Bi₂WO₆ resulted in a high quantum yield of 3.16×10^{-5} molecules/photon, which is superior to the yield of the photocatalysts currently used. High photocurrent density (0.78 mA/cm²) confirmed the excellent photoelectrochemical potential for water splitting. Hydroxyl radicals generated at the valence band and superoxide radicals at defect sites in the Bi₂WO₆ explain the excellent catalytic activity of UCNP@Bi₂WO₆. A figure of merit (FOM) reflecting important operational parameters was calculated and compared with previous reports for catalytic performance evaluation. The high FOM value of the UCNP@Bi₂WO₆ hybrid composite indicates its excellent potential for practical applications.

1. Introduction

Photocatalysis has evolved into a green technology with applications in many emerging fields [1]. The most well-known photocatalyst semiconductor materials, such as TiO₂, ZnO, ZrO₂, ZnS, and SnO₂, operate under ultraviolet (UV) radiation [2]. Visible light, which constitutes about 45% of the solar spectrum, can be used by narrow band-gap semiconductor materials, such as CdS, CdSe, Fe₂O₃, Ag₃PO₄, and C₃N₄, to generate electron-hole pairs for redox reactions [3–5]. While much attention has been focused on UV–visible (UV–vis) active hybrid photocatalysts, infrared radiation, which forms 50% of the solar spectrum, has been relatively overlooked. This substantial waste of energy is of concern and photocatalysts that can use a maximal part of the solar spectrum are clearly needed [6]. Integrating photon upconverting nanoparticles (UCNPs) with a narrow band-gap photocatalyst can potentially yield a solution to the low photon utilization of conventional materials [7]. The upconverted photons emitted in the UV–vis spectrum can be used by a photocatalyst for its activation. Composites of UCNPs and different photocatalysts, such as ZnO, TiO₂ and TiO₂/Au, have been

reported [8–11]. Due to the large band gaps, those composites use only UV photons via near infrared (NIR) upconversion. Heterojunction metal sulfides with small band gaps solved the light absorption problem. However, photocorrosion of sulfide photocatalysts and their consequent leaching is still a dilemma [12,13]. Previously reported UCNPs also suffer from distortion in the lattice configuration after photocatalyst incorporation [14]. UCNPs in combination with conventional photocatalysts such as CdS and ZnO have also been investigated [15,16]. Those catalysts were limited by their low quantum yields, due to either unsuitable band edge position or ineffective energy transfer from the core to the shell. Therefore, combinations of UCNPs and photocatalysts need to be improved by enhancing UV–vis light absorption, lowering the band gap, and ensuring excellent core@shell morphology for effective energy transfer between core and shell.

UCNPs are generally composed of three integral parts: a host matrix, sensitizer, and activator [17]. The hexagonal NaYF₄ host matrix is known for its excellent stability and NIR photon migration in the lattice [18,19]. Its low phonon energy also suppresses non-radiative relaxation and energy loss. Integrating a NaYF₄ host lattice with a sensitizer that

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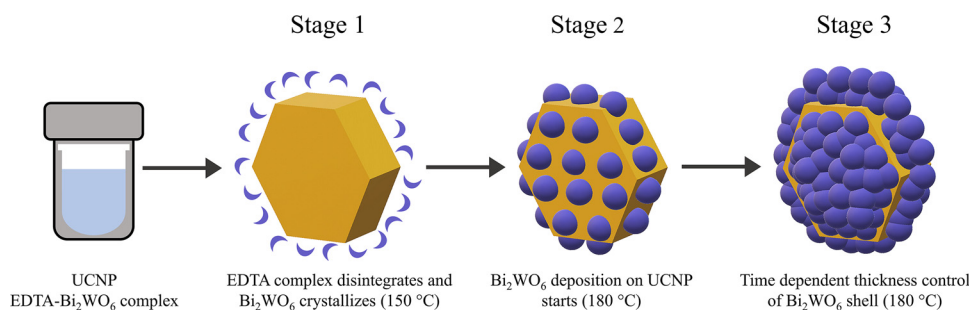


Fig. 1. Schematic of the formation and growth of the Bi₂WO₆ shell on the UCNP core.

has a large absorption cross section could form an ideal UCNP core. Trivalent ytterbium (Yb³⁺) with a relatively large absorption cross-section of $9.11 \times 10^{-21} \text{ cm}^2$ and a single excited energy level (²F_{5/2}) makes an excellent sensitizer [20,21]. Upconversion also relies on the type of activator ions in the UCNP lattice. Energy transfer upconversion (ETU) is considered to be the most efficient of the five basic mechanisms for energy transfer and photon upconversion by UCNPs, as shown in Fig. S1. Trivalent thulium ions (Tm³⁺), which have adequate intermediate energy states and a ladder-like configuration of energy levels, are appropriate for ETU [22]. The upconversion can be further improved in the UV range by doping with gadolinium ions (Gd³⁺) [23]. Lanthanides are well known for their photon upconversion properties. In this research, we embedded NaYF₄, the host matrix, with a lanthanide sensitizer (Yb³⁺) and activators (Tm³⁺ and Gd³⁺) to upconvert NIR to UV–vis light.

Bismuth tungstate (Bi₂WO₆), a visible-light-active photocatalyst, has been used to effectively degrade organic contaminants into simpler forms [24–26]. Its physical and chemical stability, as well as its excellent catalytic activity, piezo- and pyro-electricity, and non-linear dielectric sensitivity, make it an important photocatalyst [27]. The drawback of electron-hole recombination can be overcome by doping Bi₂WO₆ with a rare earth metal, which efficiently suppresses the charge recombination rate [28]. Herein, we report a nanocomposite of a Bi₂WO₆ shell with a UCNP core that can harvest visible light and NIR photons for photocatalytic applications. Most wet chemistry methods to fabricate core@shell structures involve reduction, precipitation, and deposition, which require either acidic or basic pH [29]. UCNP cores are sensitive to extreme pH conditions, and therefore, in this research, we assembled the Bi₂WO₆ shell around the core using a unique synthesis approach at a neutral/slightly basic pH. Because Bi₂WO₆ is insoluble in water at neutral pH, we synthesized an ethylenediaminetetraacetic acid (EDTA)-metal complex and achieved Bi₂WO₆ shell formation through the slow thermal decomposition of EDTA at high temperature, which resulted in Bi₂WO₆ precipitation around the UCNP core. This novel composite thus approaches the optimal utilization of UV–vis–NIR photons, thereby contributing effectively to the development of active solar photocatalysts.

Bisphenol A (BPA) is an endocrine-disrupting compound. The presence of BPA in urine, breast milk, human serum, placental tissue, and umbilical cord blood is well documented [30]. It enters environmental compartments as a contaminant during its manufacture, transport, and processing. BPA-based products also contaminate water bodies during environmental degradation [31]. In this research, we investigated the synthesis, upconversion capacity, and photocatalytic performance of the UCNP@Bi₂WO₆ nanocomposite for BPA degradation.

2. Experimental

2.1. Synthesis of NaYF₄: Yb³⁺, Gd³⁺, Tm³⁺ (UCNP core)

Eighty milliliters of 1.35 M trisodium citrate solution was prepared in deionized (DI) water. Y(NO₃)₃·6H₂O (2.8 mmol), Yb(NO₃)₃·5H₂O

(0.72 mmol), Gd(NO₃)₃·6H₂O (0.4 mmol), and Tm(NO₃)₃·5H₂O (0.08 mmol) were mixed and slowly added to the trisodium citrate solution. NaF (36 mmol) was added to the solution under vigorous stirring. After stirring for 30 min, the solution was transferred to a 140-mL Teflon-lined stainless-steel vessel. Hydrothermal reaction was carried out at 200 °C for 2 h. The white precipitates were separated by centrifuging at 6000 rpm for 10 min. The citrate-capped UCNPs were washed with DI water and methanol. Then, they were dried at 60 °C for 12 h.

2.2. Synthesis of the UCNP@Bi₂WO₆ nanocomposite

One millimole each of Bi(NO₃)₃·5H₂O and Na₂WO₄·2H₂O were added to 40 mL of 20% HNO₃ solution. The suspension was stirred for 4 h at room temperature. Four millimoles of EDTA were added to the suspension and stirred for 15 min. Then, the suspension was transferred to a round-bottom flask and heated at 90 °C on a heating mantle for complete EDTA dissolution. Water was evaporated by heating. The products were washed with water and ethanol. Subsequently, they were dried at 60 °C for 12 h. The EDTA-metal complexes were dissolved in 80 mL of DI water. The pH was adjusted to 7.5 using NaOH. The metal complexes did not precipitate at this pH because they were stabilized with EDTA. H₂O₂ (16 mmol) and urea (32 mmol) were slowly added to the EDTA-metal complex solution. After 30 min of stirring, 100 mg of the citrate-capped UCNPs were added, and the solution was autoclaved at 180 °C for 12 h. The EDTA decomposed at that high temperature, and the Bi₂WO₆ nanoparticles were assembled around the UCNP core. After the hydrothermal reaction, the product was centrifuged, washed with ethanol and water, and dried at 60 °C overnight. The nanocomposite was finally calcined at 450 °C for 4 h.

The UCNP and EDTA-Bi₂WO₆ complexes exist in a homogenous suspension at room temperature. Shell growth around the UCNP core can be divided into three stages (Fig. 1). EDTA is thermally degraded at a reaction temperature of 150 °C, and Bi₂WO₆ starts to crystallize in the reaction mixture at stage 1. The thermal disintegration of EDTA-Bi₂WO₆ was tested at 120 °C, 130 °C, and 140 °C. Little/no crystallization, however, occurred in the reaction vessel below 150 °C. Heating at 150 °C for 12 h results in little Bi₂WO₆ deposition, which suggests that a high temperature is required for uniform shell formation (Fig. S2(a)). Stage 2 starts at 180 °C and results in the deposition of Bi₂WO₆ particles on hexagonal UCNPs. UCNPs act as nucleation centers/seeds for adsorption of Bi₂WO₆ molecules. This heterogeneous nucleation results in preferential growth of Bi₂WO₆ around the UCNP core. The growth and thickness of Bi₂WO₆ shell are controlled in Stage 3. The optimal thickness of 30 nm was achieved in 12 h. The Bi₂WO₆ shell continues to grow until it reaches a maximum thickness of 85 nm (Fig. S2(b)). After that, the core@shell structure becomes unstable and starts to disintegrate (Fig. S2(c)).

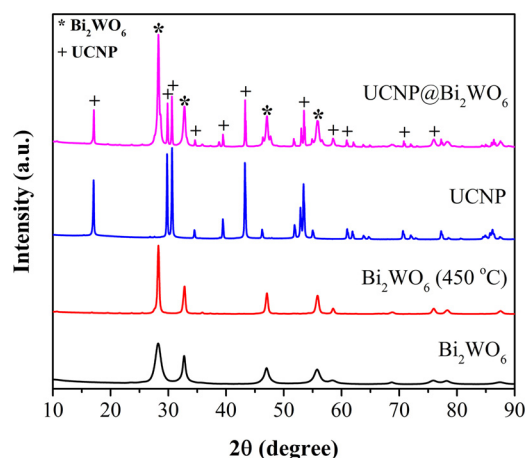


Fig. 2. XRD spectra of Bi_2WO_6 , UCNPs, and $\text{UCNP@Bi}_2\text{WO}_6$.

3. Results and discussion

3.1. XRD

Fig. 2 shows the XRD patterns of the Bi_2WO_6 , UCNPs, and $\text{UCNP@Bi}_2\text{WO}_6$ used in this research. Four distinct peaks at $2\theta = 28.3^\circ$, 32.7° , 47° , and 55.7° are characteristic of the perovskite phase of Bi_2WO_6 (JCPDS No. 75-3514). Those peak positions indicate that crystal growth occurred along the (131), (200), (202), and (133) planes of Bi_2WO_6 [32]. Broad peaks in the as-synthesized Bi_2WO_6 imply low crystallinity. To improve the crystalline phase, we calcined Bi_2WO_6 at three different temperatures, 350°C , 450°C , and 550°C (Fig. S4). The peaks were sharper and more intense at higher calcination temperatures, suggesting an increase in the crystalline phase. However, the peak intensity declined at temperatures higher than 450°C , possibly due to the sintering effect at 550°C , which resulted in the fusion of crystal boundaries [33]. Thus, all composites were calcined at 450°C in this research. The XRD spectra of UCNPs in Fig. 2 exhibit peaks at $2\theta = 17^\circ$ (100), 29.78° (110), 30.63° (101), 34.52° (200), 39.4° (111), 43.26° (201), 46.23° (210), 51.86° (002), 52.88° (300), 53.41° (211), 54.99° (102), 60.96° (112), 61.89° (220), 70.64° (311), and 77.25° (302). Those peaks can be attributed to the hexagonal β -phase of NaYF_4 (JCPDS No. 77-2042). No peaks corresponding to the NaYF_4 cubic phase ($2\theta = 27.95^\circ$, 32.72° , and 46.9°) were observed, indicating that the UCNPs existed only in the hexagonal form [34,35]. The XRD spectrum of $\text{UCNP@Bi}_2\text{WO}_6$ exhibited the peaks of both UCNPs and Bi_2WO_6 , showing that core@shell nanoparticles were successfully synthesized. The absence of any extraneous peaks in the XRD spectra confirms the crystalline purity of the synthesized composites. The crystallite sizes of Bi_2WO_6 and UCNPs, determined from Scherrer's equation, were 7.8 and 345.7 nm, respectively.

3.2. Structure and morphology

The surface and internal structure were investigated using TEM, SEM, HRTEM, and EDS-mapping. Fig. 3(a) shows the SEM image of the hexagonal UCNPs with a uniform diameter of 300–350 nm. Plate-like UCNPs formed with distinct edges and few surface defects. Their average thickness was 110–130 nm. TEM image of the UCNPs in Fig. 3(b) further confirm their excellent geometrical features with symmetrical boundaries. The size of the UCNPs determined by SEM and TEM is consistent with that calculated by Scherrer's equation using XRD. The Bi_2WO_6 shell assembled around the UCNPs core via hydrothermal treatment is shown in Fig. 3(c). The UCNPs were uniformly enveloped by the Bi_2WO_6 particles, and unbound shell particles were little to none (Figs. 3(c and d)). The thickness of the Bi_2WO_6 shell was 25–30 nm (Fig. 3(e)), which is ideal for transmitting NIR to UCNPs core.

Higher shell transmittance is vital to effective photon upconversion for catalytic applications. Interfacial connection and crystallographic features of the $\text{UCNP@Bi}_2\text{WO}_6$ composite were investigated with HRTEM. Fig. 3(f) reveals two distinct types of lattice fringes in the composite structure. The interplanar spacing of 0.31 nm corresponds to the (131) plane of Bi_2WO_6 , whereas the larger lattice spacing indicates the presence of a (100) plane of hexagonal NaYF_4 . The HRTEM results are consistent with those of XRD, confirming the crystallinity of the composite [36,37]. The spatial distribution of elements in the $\text{UCNP@Bi}_2\text{WO}_6$ composite is illustrated in Fig. 3(g–l). The relative abundance of elements is consistent with the intended percentage composition of $\text{UCNP@Bi}_2\text{WO}_6$. The densest image was formed in yttrium due to its presence in the core as the host matrix (70%). Gadolinium and ytterbium were present alongside the yttrium atoms to the extent of 20 and 18%, respectively. Bi_2WO_6 shell formation was also confirmed by the presence of bismuth and tungsten at the surface of the hexagonal UCNPs particles (Figs. 3(k and l)).

3.3. Functional groups

The FT-IR spectra are shown in Fig. 4. The absorption signals at $3200\text{--}3500\text{ cm}^{-1}$ in Bi_2WO_6 , $\text{Bi}_2\text{WO}_6\text{-EDTA}$, and the UCNPs correspond to the symmetric O–H stretching vibrations of hydroxyl groups. Similarly, the absorption between 1050 and 1450 cm^{-1} in the FT-IR spectra is caused by the O–H bending vibrations, C–O–C stretching, and C–O vibrations of hydrocarbons [38]. The peak intensities at $3200\text{--}3500$ and $1050\text{--}1450\text{ cm}^{-1}$ decreased in the calcined composites, indicating the removal of O–H groups, adsorbed water molecules, and organic impurities. The broad absorption band in the $\text{Bi}_2\text{WO}_6\text{-EDTA}$ spectrum near $2400\text{--}3400\text{ cm}^{-1}$ could result from the hydrolysis of EDTA to its acid form [39]. The $\text{Bi}_2\text{WO}_6\text{-EDTA}$ spectrum showed carbonyl (C=O) and C=C groups at 1740 and 1600 cm^{-1} , respectively. The absorption peaks associated with EDTA functional groups were absent/weakened in the Bi_2WO_6 spectrum, possibly because of the disintegration of $\text{Bi}_2\text{WO}_6\text{-EDTA}$ complexes followed by the decomposition of EDTA during the high-temperature hydrothermal treatment [40]. Splitting of the EDTA-metal complexes corroborated our synthesis approach for *in situ* assembly of the Bi_2WO_6 shell around the UCNPs core. The absorption peak at $700\text{--}800\text{ cm}^{-1}$, which is the characteristic absorption band of the W–O and Bi–O groups, appeared in spectra of the composites containing Bi_2WO_6 [41]. This peak shifted toward a lower wavenumber in the $\text{Bi}_2\text{WO}_6\text{-EDTA}$ spectrum, confirming the coordination between EDTA and Bi_2WO_6 [42]. The peaks at 1590 and 1395 cm^{-1} in UCNPs spectrum correspond to COO asymmetric stretch and CH_2 flexural vibrations [43]. The presence of these functional groups indicates successful capping of the UCNPs with citrate ligands. The characteristic absorption peak of NaYF_4 appeared at around 450 cm^{-1} in UCNPs-containing spectra. The citrate and EDTA functional groups were mostly decomposed during the hydrothermal reaction between the UCNPs and Bi_2WO_6 , as shown in the $\text{UCNP@Bi}_2\text{WO}_6$ spectrum. In the calcined $\text{UCNP@Bi}_2\text{WO}_6$ spectrum, only the characteristic absorption peaks of UCNPs and Bi_2WO_6 were observed. The remaining peaks associated with organic functional groups and impurities were eliminated during calcination.

3.4. XPS

We performed XPS analysis to understand the elemental states and chemical coordination between the UCNPs core and Bi_2WO_6 shell. Fig. 5(a) shows the $\text{Bi}4f$ spectrum of Bi_2WO_6 , with the peaks at 158.9 and 163.9 eV confirming the presence of bismuth in the Bi^{3+} oxidation state [44]. The binding energy (BE) peaks of $\text{Bi}4f_{7/2}$ and $\text{Bi}4f_{5/2}$ increased by 1 eV when Bi_2WO_6 was assembled around the UCNPs core. This shift in the BE peaks could be caused by the formation of Bi–O–Y bonds in the $\text{UCNP@Bi}_2\text{WO}_6$ composite. The absence of peaks at 156.5 and 162 eV , associated with elemental bismuth (Bi^0), indicates that the

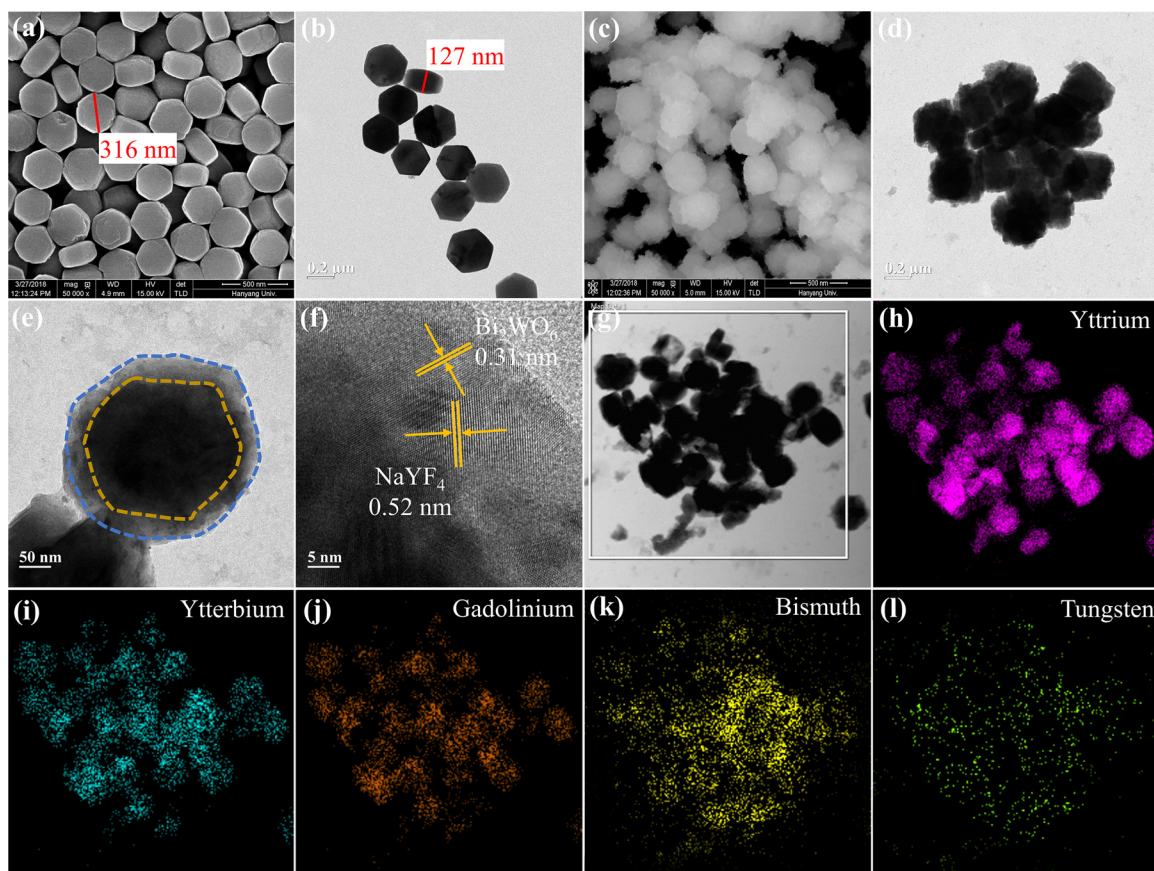


Fig. 3. (a) SEM and (b) TEM images of UCNP. (c) SEM and (d) TEM images of UCNP@Bi₂WO₆. (e) TEM image of a single UCNP@Bi₂WO₆ particle. (f) HRTEM image of UCNP@Bi₂WO₆ composite showing lattice fringe spacing of Bi₂WO₆ and NaYF₄. (g) TEM sample used for energy-dispersive X-ray spectroscopy (EDS mapping). (h–l) EDS mapping showing spatial distribution and relative abundance of elements in UCNP@Bi₂WO₆.

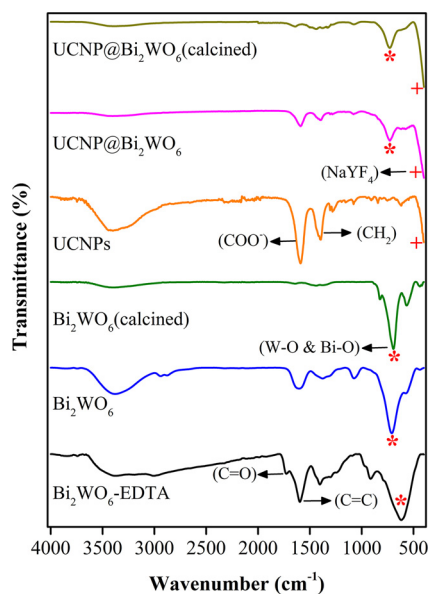


Fig. 4. FT-IR spectra illustrating important functional groups.

bismuth precursor was completely converted to Bi₂WO₆ [45]. The host matrix in the UCNP core, yttrium, revealed two BE peaks at 302.2 and 314.8 eV (Fig. 5(b)). These BE peaks correspond to the Y3p doublet, suggesting the presence of yttrium in the Y³⁺ oxidation state [46]. The electronic environment of the NaYF₄ core changed after the deposition of the Bi₂WO₆ shell. The shift in BE peaks of Y3p_{3/2} and Y3p_{1/2}

indicates that bismuth and tungsten atoms were successfully incorporated in the host NaYF₄ lattice. The BE peaks at 182.7 and 186.3 eV in Fig. 5(c) are associated with Yb³⁺ [47,48]. Likewise, the Gd3d_{3/2} and Gd3d_{5/2} spin-orbit splitting at 1187 and 1219 eV confirms the Gd³⁺ oxidation state in the UCNP@Bi₂WO₆ composite [49]. Fig. 5(d) shows the deconvoluted spectra of O1s, which yielded two distinct peaks at 530.9 and 532.5 eV. The two O1s peaks reflect the presence of multiple oxygen states in UCNP@Bi₂WO₆. The peak at 530.9 eV corresponds to oxygen bonded to metals, whereas that at 532.5 eV can be attributed to oxygen species in adsorbed water molecules. The shifting BE peaks in bismuth and yttrium, along with the multiple oxygen states, implies that the Bi₂WO₆ shell was chemically bonded with the UCNP core through electron sharing. The oxidation states of elements indicated the successful synthesis of the composite, and absence of metallic species bodes well for photochemical reactions. The complete XPS survey spectrum of the UCNP@Bi₂WO₆ composite is shown in Fig. S5.

3.5. Light-harvesting capacity

We explored the light absorption, photon-upconversion, charge-carrier separation, and photocurrent response of the UCNP@Bi₂WO₆ nanocomposite under solar and NIR illumination. First, we examined the optical properties of the composite using diffuse reflectance spectroscopy (DRS), as shown in Fig. 6(a). The Bi₂WO₆ shell exhibited strong photoabsorption in the UV-vis region, suggesting that it can utilize the direct solar photons as well as the upconverted infrared photons. The strong absorption signal around 500 nm corresponds to the band-gap energy of Bi₂WO₆, which was calculated using the Tauc equation [50]:

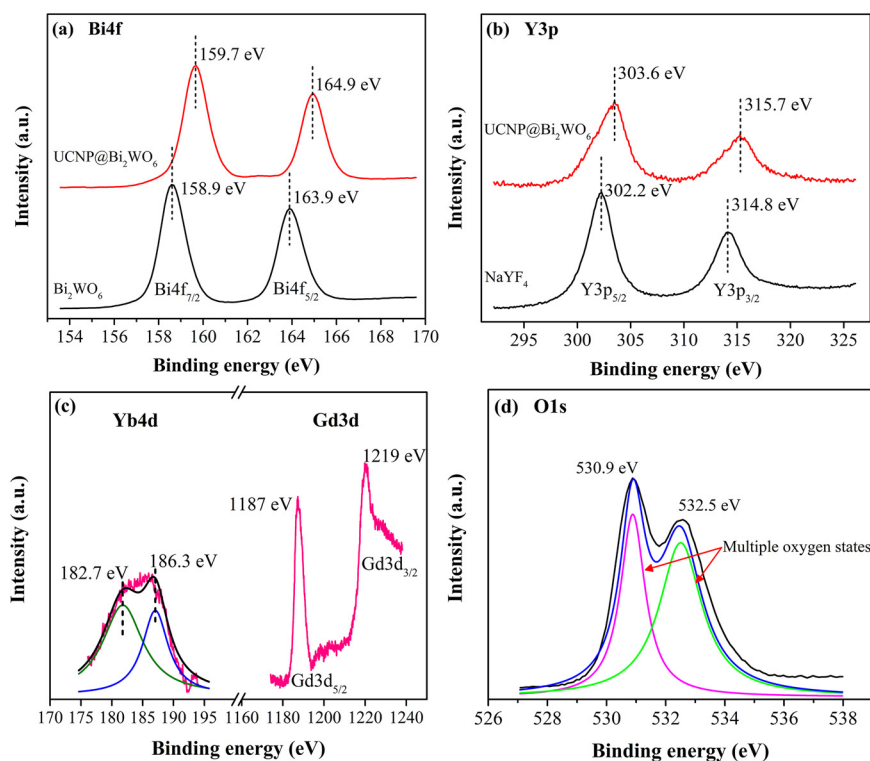


Fig. 5. XPS spectra of (a) Bi4f, (b) Y3p, (c) Yb4d and Gd3d, and (d) O1s.

$$(h\nu\alpha)1/n = A(h\nu - E_g),$$

(1)

where h is Planck's constant, ν is the vibrational frequency, α is the absorption coefficient, n refers to the type of electron transition ($n = 1/2$ for direct transitions), E_g is the band-gap energy, and A is a proportionality constant. α is directly proportional to the Kubelka-Munk function ($F(R_\infty)$) [51]. Substituting $F(R_\infty)$ in Eq. 1 gives:

$$(h\nu F(R_\infty))^2 = A(h\nu - E_g).$$

(2)

The band-gap energies of Bi_2WO_6 and $\text{UCNP@Bi}_2\text{WO}_6$, calculated by projecting the cutoff-tangent to the x-axis, were 2.63 and 2.49 eV, respectively (Fig. 6(a-inset)). Low band gap energy and high absorption in UV–vis region implies that $\text{UCNP@Bi}_2\text{WO}_6$ can utilize photons in a wide light spectrum, which results in higher quantum yield for

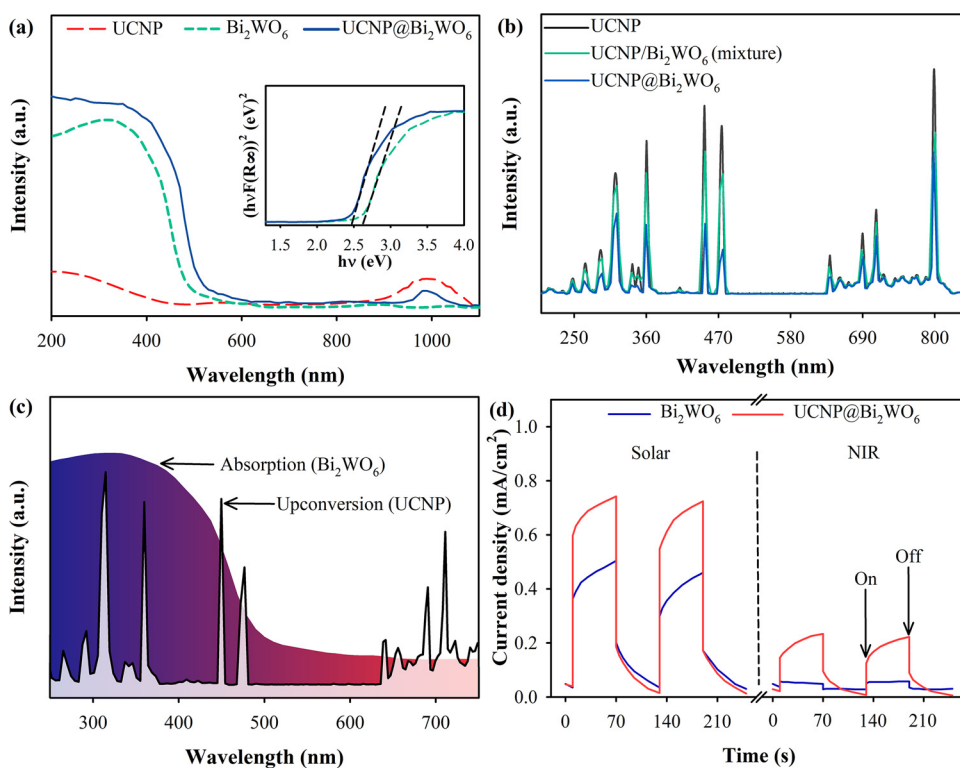


Fig. 6. (a) UV–vis–NIR absorption spectra of the nanocomposites. Inset shows the Tauc plot to determine the band-gap energy. (b) Photoluminescence spectra of the UCNPs, $\text{UCNP@Bi}_2\text{WO}_6$, and $\text{UCNP@Bi}_2\text{WO}_6$ (mixture). (c) Absorption and emission spectral overlap of the Bi_2WO_6 shell and UCNP core. (d) Photocurrent responses of the Bi_2WO_6 and $\text{UCNP@Bi}_2\text{WO}_6$ to light on-off cycles under solar and NIR light.

Table 1
Upconversion emissions and corresponding transitions of Tm^{3+} and Gd^{3+} ions.

Activator	Transition type	UC emissions (nm)	Corresponding transitions
Tm^{3+}	Two-photon	799, 690	$^3\text{H}_4 \rightarrow ^3\text{H}_6$, $^3\text{F}_3 \rightarrow ^3\text{H}_6$
	Three-photon	644, 475	$^1\text{G}_4 \rightarrow ^3\text{H}_6$, $^1\text{G}_4 \rightarrow ^3\text{F}_4$
	Four-photon	449, 360	$^1\text{D}_2 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^3\text{F}_4$
	Five-photon	339, 290	$^1\text{I}_6 \rightarrow ^3\text{H}_6$, $^1\text{I}_6 \rightarrow ^3\text{F}_4$
Gd^{3+}		313, 267	$^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$, $^6\text{I}_{7/2} \rightarrow ^8\text{S}_{7/2}$

photoreactions. The decrease in band-gap energy is due to a red shift in the absorption edge caused by the large core@shell structure and the doping-induced lattice strain [52]. The absorption spectrum of the UCNP exhibited moderate absorption in the UV and NIR regions, which corroborated the upconversion mechanism. The absorption between 900 and 1050 nm, associated with the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition, is a characteristic absorption range for Yb^{3+} ions [53]. The NIR absorption of the UCNP core was preserved in the UCNP@ Bi_2WO_6 composite. The transfer of IR photons via Bi_2WO_6 shell to UCNP core substantiated the suitability of using Bi_2WO_6 as a transmitting shell. Overall, the combination of the active core and inert photocatalyst shell yielded a hybrid composite with excellent photoresponse properties in the solar spectrum.

We investigated the photon-upconversion potential of the as-synthesized composites with photoluminescence spectroscopy (PL), as shown in Fig. 6(b). The emission bands in the blue (250–400 nm), green (450–600 nm), and red (650–800 nm) regions confirmed the upconversion of NIR photons to UV–vis photons. The emission spectrum of Tm^{3+} can be divided into four groups (Table 1). The emissions at 799 and 690 nm were generated by a two-photon transition from the $^3\text{F}_3$ and $^3\text{H}_4$ states, respectively. The three-photon transition process in the $^1\text{G}_4$ group produced peaks at 644 and 475 nm. The emission in the blue region resulted from four- and five-photon transitions from the $^1\text{D}_2$ and $^1\text{I}_6$ states, respectively [54,55]. Many emission peaks from Yb^{3+} – Tm^{3+} pairs are caused by the ladder-like structure of energy levels in Tm^{3+} , which increases the probability of multi-photon transitions. These peaks are difficult to achieve using other sensitizer–activator combinations because of their dense energy levels and inefficient non-radiative transitions [22]. The strong UV emission at 313 nm occurred due to the Gd^{3+} ions in the UCNP structure. Because of the large energy difference between the ground ($^8\text{S}_{7/2}$) and excited states ($^6\text{P}_J$), it is not possible for 980-nm photons to excite the Gd^{3+} ions. However, the excited states of Gd^{3+} were filled via an electron transition from $^3\text{P}_2$ (Tm^{3+}) to $^6\text{I}_J$ (Gd^{3+}) [56].

Light absorption and photon-upconversion can enhance catalytic activity if they interact constructively. To investigate the mutual collaboration between the above-mentioned properties, we overlapped the Bi_2WO_6 absorption spectrum with the UCNP emission spectrum (Fig. 6(c)). The wavelength of photons emitted from the UCNP corresponds to the light absorption range of Bi_2WO_6 . Therefore, the unique core@shell combination described here provides the spectral overlapping essential to the energy transfer process between the core and shell.

Energy transfer from the UCNP core to the photocatalyst shell was explored by comparing the PL intensities of UCNP, UCNP@ Bi_2WO_6 , and UCNP/ Bi_2WO_6 (mixture) (Fig. S6). The highest PL emission was exhibited by the UCNP, and it decreased after the formation of the Bi_2WO_6 shell. In the UCNP@ Bi_2WO_6 spectrum, the reductions in blue, green, and red emissions were 38%, 61%, and 11%, respectively. The marked 61% decline is caused by the overlapping of absorption band of Bi_2WO_6 with green emissions from UCNP core. The decrease in PL in the mixture of UCNP and Bi_2WO_6 was smaller, 11% and 5% in green and red emissions, respectively. These results confirmed non-radiative energy transfer, or Förster resonance energy transfer (FRET), from the UCNP core to the Bi_2WO_6 shell. FRET is an excellent, non-radiative method for transferring energy from donor to acceptor molecules. It

requires a distance of less than 10 nm between the donor and acceptor, which we achieved by growing the Bi_2WO_6 shell directly over the UCNP core [57,58]. The absorption–emission spectral overlapping and close interfacial contact promoted FRET in the UCNP@ Bi_2WO_6 . On the contrary, the large donor–acceptor distance in the UCNP/ Bi_2WO_6 (mixture) resulted in conventional radiative energy transfer. Due to this inefficient energy transfer, the PL intensity of the powder mixture of UCNP and Bi_2WO_6 was higher than that of the closely bound core–shell arrangement in the UCNP@ Bi_2WO_6 .

Potentiometric experiments were performed to investigate the charge-carrier separation in the composites (Fig. S7). The lower open circuit potential (V_{OC}) corresponds to better charge-carrier separation across heterojunctions [59]. The V_{OC} of Bi_2WO_6 , UCNP@ Bi_2WO_6 , and UCNP/ Bi_2WO_6 (mixture) was -0.24 , -0.49 , and -0.33 V, respectively. Doping Bi_2WO_6 with UCNP suppressed charge-carrier recombination, which was more pronounced in the core@shell composite than the mixture of UCNP and Bi_2WO_6 . Electron-hole separation in UCNP@ Bi_2WO_6 is imperative for catalytic applications. Fig. 6(d) shows the photoresponse performance of the synthesized composites under solar and NIR radiation. A photocurrent was generated in response to photon energy received during light cycles, which was reverted to zero in subsequent dark cycles. Bi_2WO_6 was inactive under NIR before its combination with the UCNP. The photocurrent density of the UCNP@ Bi_2WO_6 was 0.22 mA/cm^2 under NIR, which improved 3.5 times under solar radiation. The current densities of Bi_2WO_6 and UCNP@ Bi_2WO_6 were 0.43 and 0.78 mA/cm^2 , respectively. Thus, combining a UCNP core with a Bi_2WO_6 catalyst accounted for a 1.8-fold increase in the photoresponse under solar radiation. The applications of the nanocomposite explored in this research can be extended to photoelectrochemical water splitting and photocatalytic hydrogen production using natural sunlight.

3.6. BPA degradation

We evaluated the photocatalytic activity of the UCNP@ Bi_2WO_6 composite using BPA photodegradation under simulated solar and NIR radiation. As shown in Fig. 7(a), the BPA concentration dropped continuously as the reaction proceeded from 0 to 180 min in the presence of the photocatalysts. Bi_2WO_6 and the UCNP exhibited 65% and 2% BPA degradation in 180 min, respectively. Degradation reached 94% under solar illumination when the UCNP@ Bi_2WO_6 composite was used. The additional increase of 29% from Bi_2WO_6 to UCNP@ Bi_2WO_6 is associated with the enhanced use of solar light through the upconversion of unused NIR photons into active UV–vis photons. The increase in UV–vis photon population was also reflected by a two-fold increase in reaction kinetics. The observed pseudo-first-order rates were 0.0029 , 0.088 , 0.1 , and 0.19 min^{-1} for the UCNP, Bi_2WO_6 , UCNP/ Bi_2WO_6 (mixture), and UCNP@ Bi_2WO_6 , respectively (Fig. S8). Energy transfer from the core to the shell was investigated by comparing the performance of the UCNP@ Bi_2WO_6 with that of the mixture of the UCNP and Bi_2WO_6 catalyst. The former showed 21% higher BPA degradation, substantiating the non-radiative energy transfer between the core and shell. The low performance of the UCNP/ Bi_2WO_6 (mixture) can be attributed to the energy loss caused by the radiative energy transfer between donor and acceptor molecules.

Photon upconversion and its role in enhancing photocatalytic activity was verified by our test of BPA degradation under NIR radiation (Fig. 7(b and c)). Taken alone, NIR radiation, UCNP, and Bi_2WO_6 failed to degrade BPA. Bi_2WO_6 exhibited BPA degradation with solar radiation, but it was inactive under NIR. Photodegradation with NIR was observed when Bi_2WO_6 was combined with the UCNP. The upconverted NIR photons were used by both the UCNP@ Bi_2WO_6 and UCNP/ Bi_2WO_6 (mixture) to degrade 51% and 26% of BPA, respectively, in 10 h. The reaction rates under NIR were much slower than those observed under solar radiation. For example, the reaction rate with UCNP@ Bi_2WO_6 was 190 times higher under solar radiation than NIR

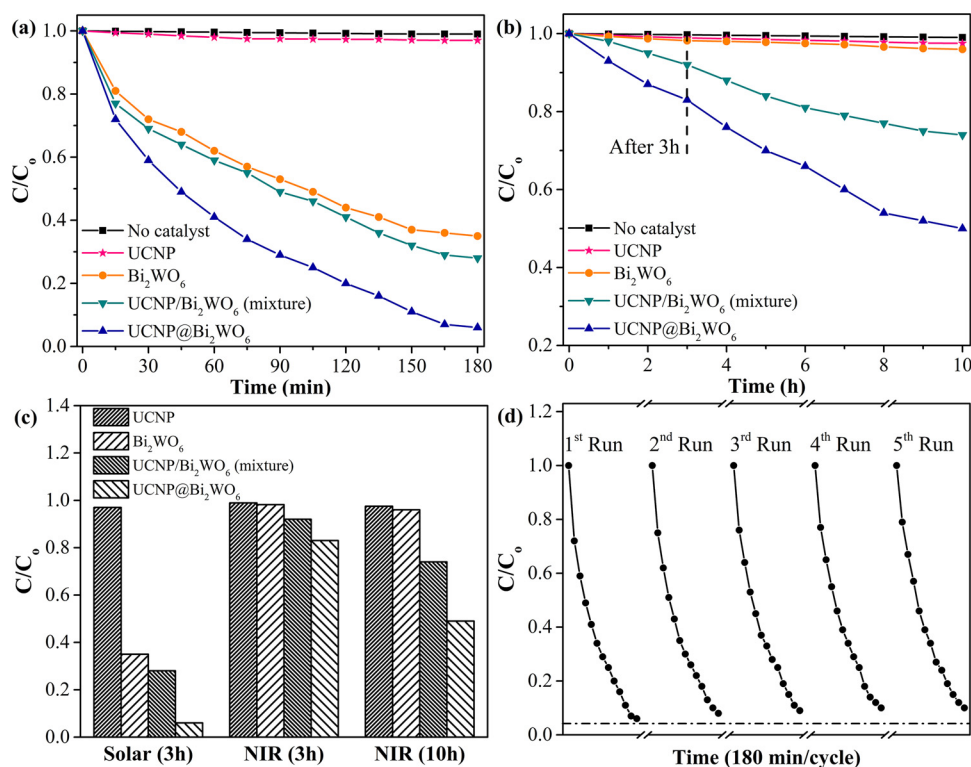


Fig. 7. Photocatalytic performance of composites under (a) solar and (b) NIR irradiation. (c) Comparison of BPA degradation under visible spectrum and NIR radiation by various composites. (d) Photocatalytic degradation of BPA in five consecutive cycles under solar irradiation.

because of the ability to exploit UV–vis as well as NIR photons.

The stability and reusability of UCNP@ Bi_2WO_6 nanocomposite are important for practical applications. We demonstrated the photoactivity of recycled composites for five successive BPA degradation cycles, as shown in Fig. 7(d). The photocatalyst, with a 5% difference from the first run, exhibited 89% BPA degradation after the fifth cycle. Thus, the UCNP@ Bi_2WO_6 composite is reusable and is not deactivated by extended exposure to UV–vis–NIR radiation. The structural stability of the composite was investigated by XRD, FT-IR, and XPS analyses of the recycled catalyst (Fig. S9). The XRD spectra of the pure and recovered composite were almost identical, with only minor changes in peak heights. Peaks at $2\theta = 37^\circ$, 45° , and 49° , corresponding to elemental bismuth were not observed, which confirmed the integrity of the Bi_2WO_6 shell [60]. The FT-IR spectra did not exhibit any redundant absorption peaks. The peaks associated with the inter-band transitions of bismuth ($990\text{--}1100\text{ cm}^{-1}$) were absent [61]. The stability of Bi_2WO_6 was further substantiated by the XPS spectra shown in Fig. S9(c). The binding energy of $\text{Bi}4f_{7/2}$ and $\text{Bi}4f_{5/2}$ was the same in the pure and recycled photocatalysts. The absence of peaks at 156.5 and 162 eV, associated with elemental bismuth (Bi^0), indicated that bismuth sustained the photocatalytic reactions.

3.7. Photocatalytic mechanism

The reaction mechanism of this novel UCNP@ Bi_2WO_6 composite is illustrated in Fig. 8. Bi_2WO_6 with a narrow band gap (2.49 eV) is activated directly by solar illumination and indirectly by upconverted photons from the UCNP core. Upon irradiation, the sensitizer (Yb^{3+}) gets excited and transfers energy to the activators (Gd^{3+} and Tm^{3+}) through dipole–dipole resonant interactions [22]. Subsequently, the activators are relaxed non-radiatively and give energy to their neighboring Bi_2WO_6 catalyst molecules. The non-radiative energy transfer is much more efficient than the conventional radiative process, which suffers from inevitable energy loss. However, non-radiative energy transfer demands sufficient spectral overlap and minimal distance

between the donor and acceptor [62]. The novel design of the core@shell composite in this study meets both those conditions. The absorption band of Bi_2WO_6 overlaps with the emissions from the UCNP core in the UV–vis range (Fig. 6(c)), and direct growth of the Bi_2WO_6 over the UCNP core makes the donor–acceptor distance negligible. This appropriate spectral overlap and close donor–acceptor contact form the basis for non-radiative energy transfer between the core and shell.

Radical scavenging experiments were performed to investigate the role of reactive oxygen species (ROS) in BPA photodegradation. As shown in Fig. S10, BPA degradation was significantly suppressed by TBA, suggesting a strong involvement of hydroxyl radicals ($\cdot\text{OH}$) in the photochemical reaction. By contrast, 65% of the BPA was degraded in the presence of BQ, a trapping agent for the superoxide radical ($\cdot\text{O}_2^-$). The scavenging experiments thus imply the major role of $\cdot\text{OH}$ radicals in BPA degradation. To better understand ROS generation by the Bi_2WO_6 photocatalyst, we determined the conduction band (CB) and valence band (VB) edge potentials using Butler and Ginley's method [63]:

$$E_{\text{VB}} = X - E^\circ + 0.5E_g \quad (3)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (4)$$

where E_{CB} is the CB potential, E_{VB} is the VB potential, E° is the energy of electrons versus the hydrogen scale (4.5 eV), E_g is the band-gap energy, and X is the absolute electronegativity of Bi_2WO_6 . The theoretically calculated VB and CB edge potentials were verified experimentally using ultraviolet photoelectron spectroscopy (Fig. S11). The $\cdot\text{OH}$ radicals are produced at the VB of Bi_2WO_6 because its VB potential (2.7 eV) is higher than the $\text{H}_2\text{O}/\cdot\text{OH}$ redox potential (2.4 eV). The scavenging experiments indicate the presence of $\cdot\text{O}_2^-$ radicals; however, the CB edge potential of Bi_2WO_6 (0.21 eV) is not low enough for $\text{O}_2/\cdot\text{O}_2^-$ conversion (-0.05 eV). Based on the results of radical trapping and band edge calculations, we propose an indirect two-step route for $\cdot\text{O}_2^-$ generation. Previous studies showed that intrinsic defects and vacancies can lead to the formation of localized acceptor states (V_D) [64]. These

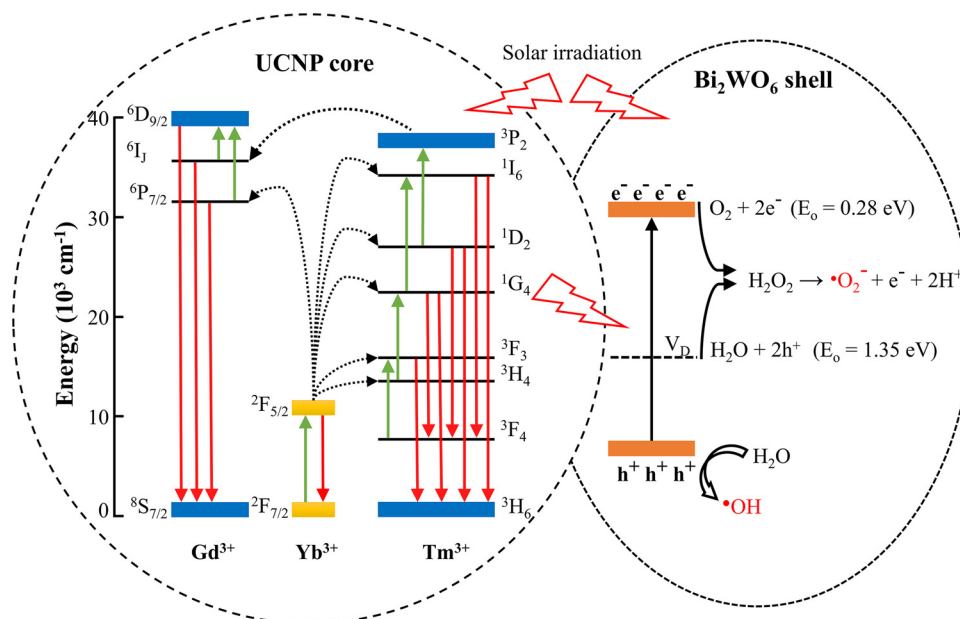


Fig. 8. Schematic illustration of energy levels and transitions in the UCNP core and transfer of energy from UCNP to Bi_2WO_6 to produce reactive oxygen species.

Table 2

Performance evaluation of photocatalyst systems for organic contaminant degradation.

No.	Photocatalyst	Contaminant	Light source	Time (min)	Energy consumption (Wh/ μmole)	Catalyst dosage (g/L)	Quantum yield (molecules/photon)	Figure of merit	Reference
1.	g- C_3N_4 /CdS/RGO	Rhodamine B	UV	20	47.9	0.4	1.98×10^{-6}	100.0	[68]
2.	g- C_3N_4 /RGO	Rhodamine B	UV	30	71.9	0.4	1.32×10^{-6}	44.4	[68]
3.	g- C_3N_4 /CdS/RGO	Rhodamine B	Vis	60	47.9	0.4	1.26×10^{-6}	33.3	[68]
4.	BN/CdS	Rhodamine B	Vis	90	14.1	0.6	5.64×10^{-6}	30.7	[69]
5.	g- C_3N_4 /BiOI	Rhodamine B	Vis	50	121.0	0.1	5.00×10^{-7}	25.3	[70]
6.	g- C_3N_4 /CdS	Rhodamine B	UV	40	95.8	0.4	9.92×10^{-7}	25.0	[68]
7.	RGO/CdS	Rhodamine B	UV	40	95.8	0.4	9.92×10^{-7}	25.0	[68]
8.	$\text{Ag}_3\text{PO}_4/\text{CeO}_2$	Rhodamine B	Vis	60	65.3	0.4	9.25×10^{-7}	24.5	[71]
9.	$\text{BiVO}_4/\text{Ag}_3\text{VO}_4$	Rhodamine B	Vis	20	41.6	1.0	1.45×10^{-6}	18.4	[72]
10.	RGO/CdS	Rhodamine B	Vis	150	119.8	0.4	5.05×10^{-7}	5.3	[68]
11.	TiO_2	Reactive black	UV	300	9.7	2.0	9.81×10^{-6}	13.2	[73]
12.	TiO_2	Patent Blue VF	UV	80	22.9	1.0	3.82×10^{-6}	20.9	[74]
13.	$\text{Bi}_2\text{S}_3/\text{TiO}_2$ /RGO	Methylene blue	Vis	90	39.3	0.4	1.54×10^{-6}	54.2	[75]
14.	ZnS/CdS	Methylene Blue	Vis	180	148.1	0.1	4.08×10^{-7}	34.5	[76]
15.	CdS	Methylene Blue	Vis	360	533.1	0.1	1.13×10^{-7}	4.8	[76]
16.	$\text{WO}_3/\text{NiWO}_4$	Methylene blue	UV	400	41.2	0.6	2.31×10^{-6}	5.7	[77]
17.	TiO_2	Methylene Blue	Vis	360	253.9	0.1	2.38×10^{-7}	10.1	[73]
18.	$\text{BiVO}_4/\text{Ag}_3\text{VO}_4$	Methyl violet	Vis	40	72.5	1.0	8.34×10^{-7}	5.3	[72]
19.	CdS	Methyl red	UV	180	35.1	1.0	2.34×10^{-6}	4.8	[78]
20.	Graphene/ TiO_2	Methyl Orange	UV	20	34.6	0.6	1.76×10^{-6}	28.1	[79]
21.	CuO/BiVO_4	Bisphenol A	Vis	5	794.0	0.5	1.73×10^{-7}	9.3	[80]
22.	g- C_3N_4	Bisphenol A	Vis	60	68.5	0.5	1.91×10^{-6}	7.5	[81]
23.	rGO/ TiO_2	Bisphenol A	UV	120	40.6	1.0	3.22×10^{-6}	1.6	[82]
24.	$\text{SrTiO}_3/\text{Ag}/\text{AgCl}$	Bisphenol A	Vis	30	35.3	0.5	3.70×10^{-6}	28.9	[83]
25.	$\text{Ag}/\text{C}_3\text{N}_4$	Bisphenol A	Vis	240	291.8	0.6	4.48×10^{-7}	0.2	[84]
This study		Bisphenol A	Solar	180	4.7	0.3	3.16×10^{-5}	72.2	

acceptor states are higher than the original valence band minimum and can provide additional sites for photochemical reactions. As shown in Fig. 8, H_2O and O_2 were first converted to H_2O_2 at V_D and CB, respectively. In the second step, H_2O_2 disintegrated under irradiation, producing the $\cdot\text{O}_2^-$ radicals that were detected during the scavenging experiments [65]. The UV–vis–NIR response of the composite that generated $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals resulted in high BPA degradation.

3.8. Performance evaluation

Important photocatalytic characteristics, such as the type of contaminant, light source, product yield, contaminant load, mass of catalyst, energy consumed, and final product, can vary from one study to

another. Previously, quantum yield (QY) was used to evaluate the performance of photocatalyst systems [66,67]. However, QY alone is insufficient, therefore, we calculated a figure of merit (FOM) based on important operational parameters, as follows [38]:

FOM

$$= \frac{\text{Product obtained (L)}}{\text{Catalyst dosage (g/L)} \times \text{Time (h)} \times \text{Energy consumption (Wh}/\mu\text{mole)}} \quad (5)$$

For simplification, the highest FOM obtained was set to 100. Then, all the other FOMs were calculated proportionally. Modified FOMs with corresponding system QYs are listed in Table 2. The FOMs show both a direct and an inverse relationship with the QYs of photocatalysts. For

instance, the QY of ZnS/CdS is 7 times smaller than that of the SrTiO₃/Ag/AgCl composite, but the FOM of the former is larger. On the contrary, the FOM/QY ratios of g-C₃N₄/RGO and ZnS/CdS show a direct relationship. The two different trends accentuate the importance of the FOM to categorize system performance in a broad context. The highest FOM (100) was observed for the g-C₃N₄/CdS/RGO composite under UV, which dropped to 33 under visible light. The FOM of the UCNP@Bi₂WO₆ composite (72) is smaller than that of the g-C₃N₄/CdS/RGO composite, but the irradiation source for the latter was UV, which forms only 5–6% of the solar spectrum. Comparing the performance of the g-C₃N₄/CdS/RGO composite in UV–vis light with that of the UCNP@Bi₂WO₆ under solar radiation indicates that the novel nanocomposite presented in this research can offer great utility for solar-driven photochemical reactions.

4. Conclusion

We synthesized a novel composite of UCNP@Bi₂WO₆ and presented a new synthesis method to overcome the disintegration of UCNP during photocatalyst shell formation. Neither the UCNPs nor the Bi₂WO₆ exhibited catalytic activity in NIR, but the UCNP@Bi₂WO₆ degraded BPA in low-energy NIR radiation. FRET was used for energy transfer because of the absorption/emission spectral overlapping and close interfacial core/shell contact. 'OH and 'O₂^{•−} radicals were generated in the reaction mixture under NIR, which accounted for the increase in the composite's photoactivity under solar radiation. The high photocurrent response suggests that UCNP@Bi₂WO₆ could be used for photoelectrochemical water splitting as well. Our results provide a framework for future studies of NIR-based photocatalysts for complete exploitation of solar energy.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.10.074>.

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